PUFF-BY-PUFF DETERMINATION OF GAS PHASE ACETALDEHYDE, HCN, NO AND CO USING FT-IR SPECTROMETRY.

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SUMMARY

A multi-component, quantitative FT-IR spectrometric method has been developed for the simultaneous determination of the concentrations of acetaldehyde, HCN, NO, and CO present in gas-phase cigarette smoke. A 50 mL portion of gas-phase cigarette smoke from a five-port-smoking machine is trapped in a sample loop, diluted with nitrogen, and transferred to a simple transmission gas cell positioned in the sample compartment of a table-top FT-IR spectrometer. Thirty seconds of the standard one minute smoking cycle are used to collect an infrared spectrum. The remainder of the time period between puffs is used to flush the gas cell with nitrogen. The infrared spectrum contains absorption lines specific for each of the analyte gases. Calibration curves were obtained by relating selected absorption peak areas to known concentrations of the individual gases. The spectral response of an FT-IR spectrometer is stable and frequent calibration is not required. The wavelength accuracy of an FT-IR spectrometer permits automated and reproducible measurement of absorption peak areas. A micro-computer is used to control the flow of smoke and purge gas through the gas cell, and to analyze the spectral data. The entire analytical procedure is designed for simple and reliable operation. The FT-IR spectrometer replaces and provides comparable results to individual instruments currently used for the analysis of each gaseous component.

INTRODUCTION

An FT-IR spectroscopic technique has been developed for the simultaneous, quantitative determination of acetaldehyde, hydrogen cyanide, nitric oxide, and carbon monoxide in gas-phase mainstream (MS) cigarette smoke. Puff-by-puff concentrations for each of the gases were determined by fitting the peak areas of selected absorption lines, present in the MS smoke spectrum, to calibration data. Calibration curves were established by flowing a series of concentrations of reference gases through the sample compartment of the FT-IR spectrometer.

This new method replaces a system that utilized a separate analysis procedure for each gas: a non-dispersive infrared spectrophotometer for CO; an oxides of nitrogen analyzer that detects the chemiluminescence of the reaction product of NO and ozone; and a water scrubbing tower for the entrapment of HCN and acetaldehyde prior to their subsequent colorimetric determinations by an AutoAnalyzer™ procedure. Each of these methods requires daily calibration. The focus in the development of this new analysis procedure was to design a system that is accurate, reliable,

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low-cost, and automated. Recent advances in FT-IR spectrometer instrumentation has made available low-cost, rugged, low-maintenance systems well suited for reliable analytical laboratory applications. The FT-IR spectrometer is equipped with a maintenance-free, room-temperature, deuterated triglycine sulfate (DTGS) detector, and simple transmission gas cell with replaceable, low-cost KCl windows. An interface delivers the smoke from the smoking machine to the FT-IR spectrometer and purges the sample cell between puffs. The entire analysis procedure, with the exception of the lighting of the cigarettes is automated.

ANALYSIS SYSTEM DESIGN

Cigarettes were smoked on a five-port smoking machine using a 35-mL, 2-second duration puff, every 60 seconds. Cigarettes were smoked to a butt length of 3 mm from the tipping paper for filtered cigarettes. The environmental smoking conditions of temperature and relative humidity were maintained at 24.° C and 60% relative humidity. The smoke passes through a standard Cambridge filter pad (0.3 micron pore size) in a Lucite® filter assembly. The 175 mL output of the smoking machine is pushed through a sample loop connected to the interface of the smoking machine and FT-IR spectrometer (Figure 1). The opposite end of the sample loop is open to an atmospheric pressure vent. After a short delay period of 2 seconds, the sample loop is connected to the analysis loop. The analysis loop consists of the sample loop, a peristaltic pump, and the gas cell in the sample compartment of the FT-IR spectrometer. The pump is activated and the smoke sample, diluted with nitrogen, circulates through the analysis loop for 35 seconds. The sample spectrum is obtained during this time. The analysis loop is purged with high pressure nitrogen during the last 20 seconds of the one minute smoking cycle. The timing of the smoking cycle, pump activation, sample-scan period, and valve operation is controlled by a programmable controller. The FT-IR spectrometer computer communicates with the smoking machine programmable controller and analyzes the data at the end of the smoking cycle.

The analysis sequence is initiated by the operator entering the program name. A spectrum is then obtained of the nitrogen purged sample cell. This spectrum is used as a background for the sample spectra. Experimental effects of factors such as variation in source intensity, contamination of the gas cell windows, or misalignment of the gas cell are eliminated by dividing sample spectra with a background spectrum acquired immediately prior to the analysis. A report is generated at the end of the analysis detailing the puff-count for each port of the smoking machine, the concentrations of each of the analytes per puff, and a total concentration for each cigarette. Sample names are entered into the program by a bar-code reader. The FT-IR computer is interfaced to a mainframe computer where analysis data are stored.

A Laser Precision Analytical RFX-30 series 2 cm^{-1} FT-IR spectrometer is used. The spectrometer is controlled by an IBM PC/AT compatible computer. An important feature of the spectrometer is its permanently-aligned, refractively scanned interferometer with mechanical bearings. An air-cooled source is used.
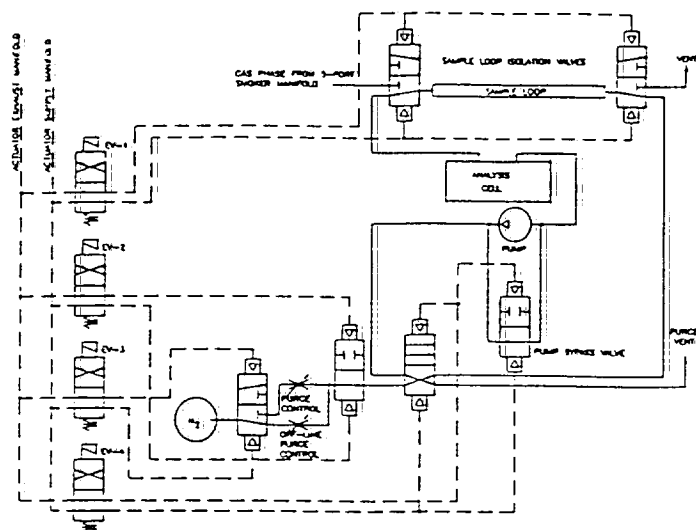
Figure 1: Valve EV-1 when actuated supplies air to drive the sample isolation valves, opening the sample loop to the discharge of the 5-port smoker's exhaust. Valve EV-2 turns the nitrogen supply off when actuated. Valve EV-3 routes the nitrogen supply through a large throttling valve when actuated, supplying a high volumetric flow rate through the sample loop and analysis cell during on-line purging. When deactuated, it routes the nitrogen supply through a small throttling valve to provide a constant low volume purge during system down periods. Valve EV-4 closes the sample-analysis loop when actuated, and closes the pump by-pass valve. When deactuated, it allows the desired purge flow of nitrogen to flow through the sample-analysis loop, bypassing the pump.
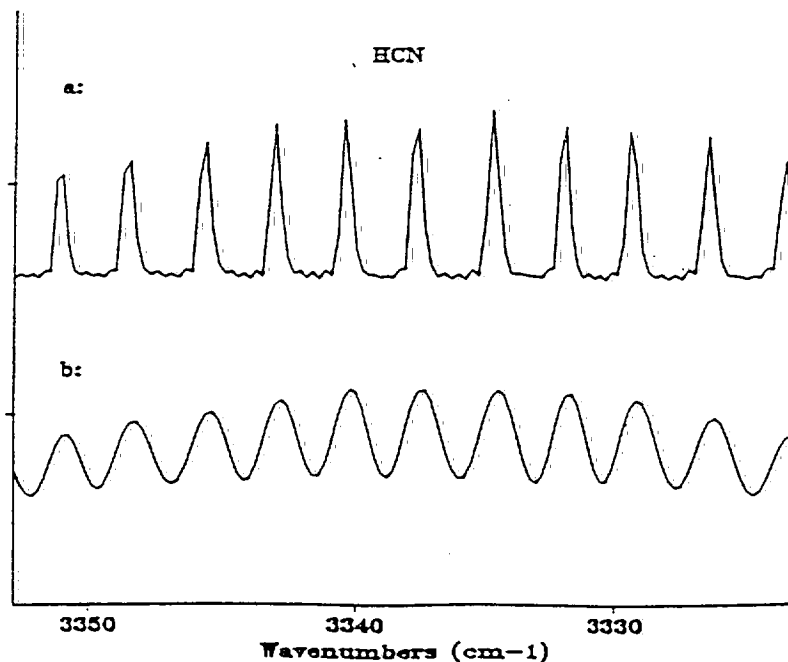

Figure 2: a: Spectrum of HCN acquired at 0.5 cm^{-1} resolution. b: Spectrum of HCN acquired at 2 cm^{-1} resolution.

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A 15-cm pathlength, single-path, transmission gas cell is located in the sample compartment of the spectrometer. The gas cell is equipped with screw-on end caps that contain the KCl windows. A reference spectrum of the gas cell with new windows is stored for comparison with a spectrum of the gas cell after prolonged use to determine when the windows need to be replaced. The gas lines to the sample cell are connected at the sample compartment wall by push-button operated quick-disconnect fittings.

RESULTS AND DISCUSSION

There are two main considerations in the use of a FT-IR spectrometer for quantitative analysis (1). The first is that the instrument must have an adequate signal to noise (S/N) ratio to allow for an accurate determination of absorption line peak areas at the minimum concentrations to be analyzed. Second, the resolution must be adequate to resolve individual analyte absorption lines from those of other infrared absorbing gases present in smoke. The two performance parameters are related in that an increase in resolution decreases the S/N ratio. The S/N ratio of an FT-IR spectrometer decreases with the square root of the number of individual scans that are coadded. For this application, the number of scans that can be collected is limited by the 60 second smoking cycle of the smoking machine.

The signal, i.e., the absorption line peak height of the analyte, is controlled by the amount of sample delivered and the pathlength of sample cell. Most low-molecular weight gases exhibit a series of narrow absorption lines as shown in Figure 2 for hydrogen cyanide. For quantitative analysis of most gas samples, the analyte concentrations must be low so that the peak areas are linearly, or approximately, linearly related to concentration. The effect of absorption levels on the linearity of peak area versus concentration is shown in Figure 3. Low-cost FT-IR spectrometers are generally limited to 2 cm^{-1} resolution. Absorption peaks that are narrower than 2 cm^{-1} appear to have a peak width of 2 cm^{-1} when collected at 2 cm^{-1} resolution (Figure 2). The net area of the peak remains the same but there is significant loss in peak height. It is for this reason that peak areas, rather than peak heights, are used for determining the concentration of the gas samples. Sample data were collected at 2 cm^{-1} resolution. This is adequate to resolve each of the analyte gases from interfering peaks. Less resolution is not adequate to resolve the NO absorption peaks from the surrounding water vapor absorption peaks.

Calibration data were obtained by mixing reference gases with nitrogen using a mass flow control system. Plots of peak area versus concentration are shown in Figure 4. Wavelengths used for each gas and the calibration equations are given in the legend of Figure 4. The corresponding regions of the smoke spectrum along with the reference gas spectra are shown in Figure 5. Acetaldehyde has a broad absorption line and is linear over a wide range in concentrations. The levels of NO are sufficiently low that a linear relationship is found over the range of concentrations encountered in cigarette smoke. A simple linear fit of the calibration data is used to determine the levels of these two cases in cigarette smoke. The relationship
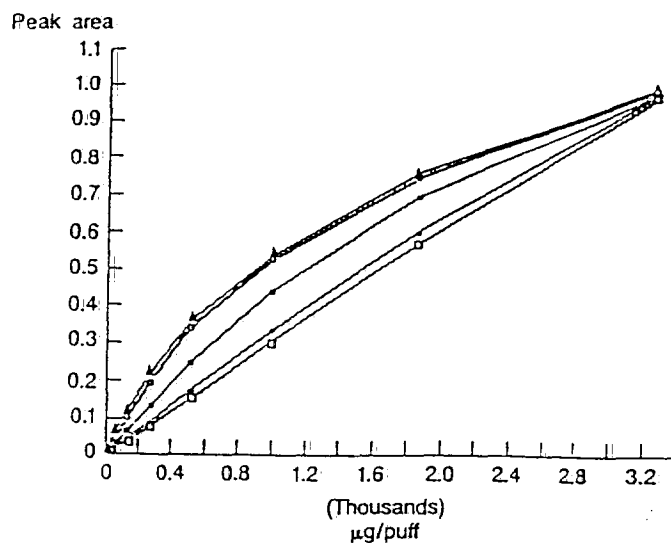
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Effect of CO Band Selection

Figure 3: All peak areas are normalized to the peak area of the most concentrated sample. □: peak 2230.3 cm⁻¹ ; •: peak 2221.5 cm⁻¹ ; ■: peak 2203.3 cm⁻¹ ; ○: peak 2193.3 cm⁻¹ ; Δ: peak 2176.2 cm⁻¹ . A spectrum of carbon monoxide is shown in Figure 5.

between the peak areas of CO and HCN and concentration are non-linear. A second-order polynomial fit of the data is used to determine the levels of CO and HCN. The small CO absorption lines that vary linearly with concentration were not used. They appear in regions of smoke spectrum that overlaps with CO_2 or carbonyl sulfide.

The HCN peak is adjacent to a CO_2 peak. The concentration of CO_2 in smoke is high and the CO_2 peak slightly overlaps the HCN peak (Figure 5d). To eliminate this interference, a scaled subtraction of a reference spectrum of CO_2 is made from the sample spectrum. The scaling factor is determined by the ratio of CO_2 sample peak height to that of the reference spectrum. The wavelength accuracy of FT-IR spectrometers, based on the wavelength of an internal helium-neon laser, allows for accurate subtraction of spectra. This wavelength accuracy also assures that the peak areas of the analyte gases can be reproducibly determined automatically from computer stored wavelengths.

Table I lists the results from the analysis of 2R1F, 2R1, and 1R4F Kentucky reference cigarettes by both the FT-IR and established procedures. The two analysis techniques demonstrated excellent agreement for CO and NO. These gases were determined by direct gas phase analysis by both systems. The comparison was not as good for HCN, and acetaldehyde. The FT-IR procedure uses direct gas-phase analysis for these components, whereas the established procedure uses an AutoAnalyzer procedure following extraction in a water tower. The differences in values for the latter gases may be attributed to the uncertainties introduced by water extraction and chemical complexation prior to analysis utilized in the established

Acetaldehyde Calibration

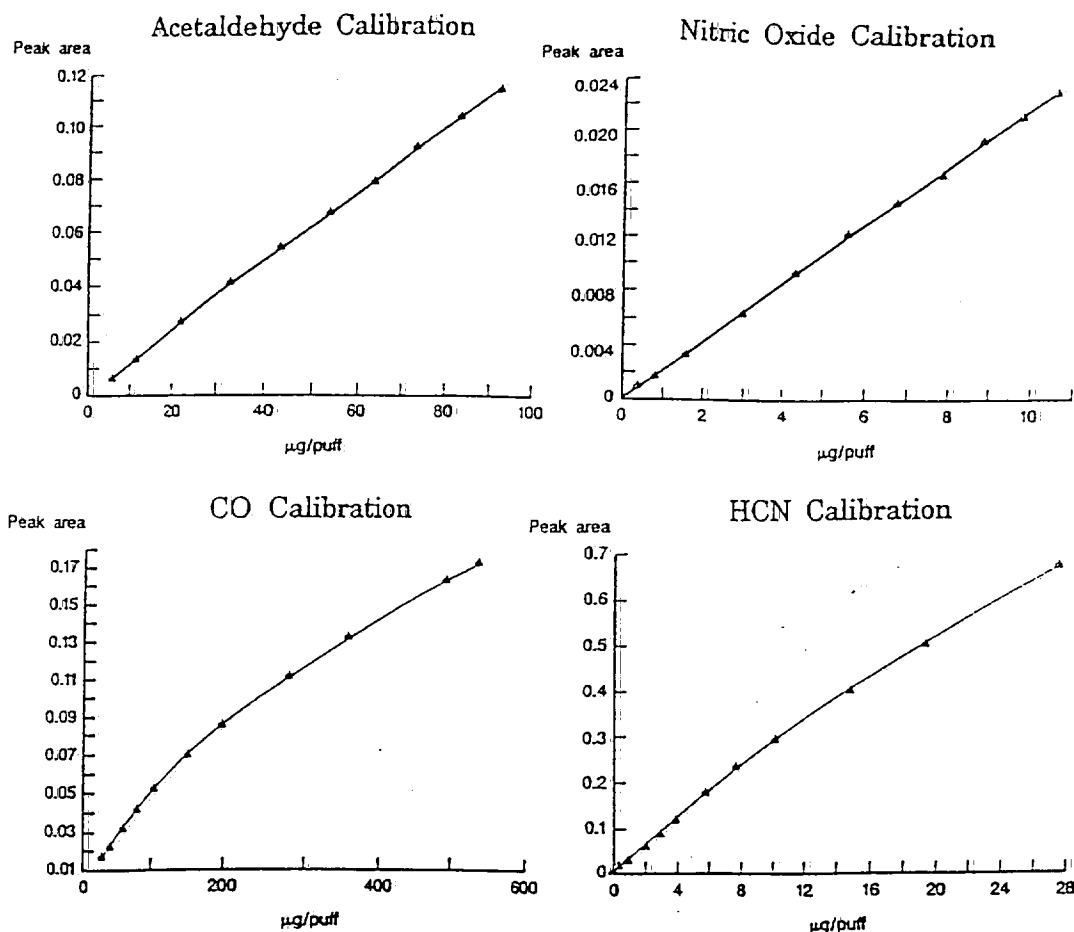## Nitric Oxide Calibration

CO Calibration

HCN Calibration

Figure 4: Concentrations of the reference gases are given in μg/puff. The smoke samples were diluted by a factor of ca. 7. Therefore, the effective concentration range, as applied to the smoke samples, is 7 times the values shown. The symbols represent experimental data. Three values are shown for each concentration. The solid line is the calibration curve derived from the experimental data. Acetaldehyde: Linear fit, $m = 1.29e-3$, $b = 0$, for concentration = m*peak area + b. Area of integration: 2738 to 2729.5 cm^{-1}, with a baseline drawn from 2766 to 2715 cm^{-1}. NO: Linear fit, $m = 2.17e-3$, $b = 0$. Areas of integration: 1904.6 to 1901.8 cm^{-1}, same values used for baseline; 1901.7 to 1898.7 cm^{-1}, sample values used for baseline; 1855.0 to 1851.8 cm^{-1}, same values used for baseline. HCN: Second order polynomial fit concentration $= 17.5x^2 + 28.9x + 0.02$, x = peak area. Area of integration: 716.7 to 710.4 cm^{-1}, same values used for baseline. CO: Second order polynomial fit: concentration $= 9987x^2 + 1328x + 4.93$. Area of integration: 2141.1 to 2137.5 cm^{-1}.
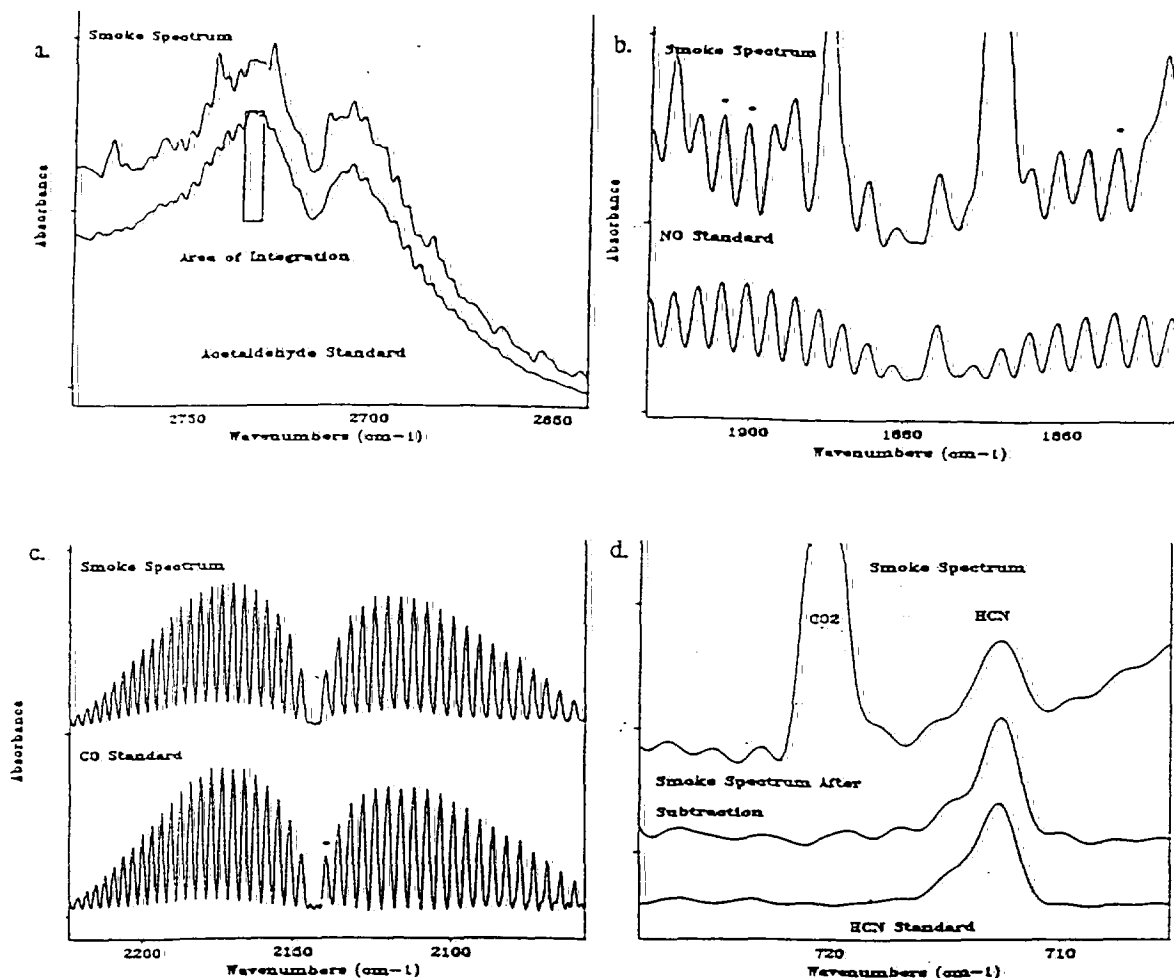
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Figure 5: a: Acetaldehyde. The box shows the area integration. b: Nitric oxide. The * indicates the peaks used for analysis. c: Carbon monoxide. The * indicates the peak used for analysis. d: Hydrogen cyanide.

procedure. Reanalysis of the reference cigarettes by the FT-IR method after 10 days produced results within 7% of those listed in Table I.

CONCLUSIONS

The FT-IR method provides a means of using a single instrument system to determine the concentrations of acetaldehyde, HCN, NO and CO in cigarette smoke. FT-IR spectrometers are rugged and require very little maintenance. A strong point in the favor of the FT-IR method is that the analysis of other gases present in smoke could be added in the future by changes in software and collection of appropriate calibration spectra.

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Table I

Comparison of New Method Versus Current Method

Sample	CO mg/cig	NO µg/cig	CH₃CHO µg/cig	HCN µg/cig	Puff Count
2R1F					
New	20.3	295	1192	184	10.5
Current	20.1	282	1051	214	10.0
% Difference	+1	+5	+13	-14	
1R4F					
New	10.5	279	670	72	8.9
Current	10.7	285	646	102	9.1
% Difference	-2	-2	+4	-29	
2R1					
New	20.9	297	1235	232	12.4
Current	21.0	300	1147	251	12.3
% Difference	-1	-1	+8	-8	

Where CH₃CHO column shows CH_3CHO.

REFERENCES

1.   P. R. Griffiths and J. A. de Haseth. Fourier Transform Infrared Spectrometry. John Wiley & Sons, Inc., USA, 1986, 338-368.

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